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AUTOMATED ANODIC STRIPPING VOLTAMMETRY FOR THE ANALYSIS OF COPP--ETC(U)
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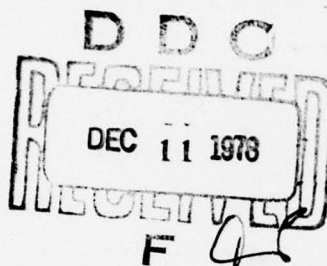
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Technical Report 243

AUTOMATED ANODIC STRIPPING VOLTAMMETRY FOR THE ANALYSIS OF COPPER, ZINC, LEAD AND CADMIUM FOR ENVIRONMENTAL MONITORING

P Kenis
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June 1978

Research and Development Report: October 1975 - April 1977

Prepared for
Naval Facilities Engineering Command

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This work was performed by the Chemistry and Environmental Sciences Branch.
It was supported by the Naval Facilities Engineering Command under Work Request
No. N00025-77-WR-00047.

Released by
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 14 NOSCTR-243	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 9
4. TITLE (and Subtitle) 6 AUTOMATED ANODIC STRIPPING VOLTAMMETRY FOR THE ANALYSIS OF COPPER, ZINC, LEAD AND CADMIUM FOR ENVIRONMENTAL MONITORING		5. TYPE OF REPORT & PERIOD COVERED Research and Development <i>rept.</i> October 1975-April 1977
7. AUTHOR(s) 10 P. Kenis, A. Zirino, C. Clavell		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, California 92152		8. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Facilities Engineering Command Washington, DC		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS N00025-77-WR-0047
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 22p.		13. REPORT DATE June 1978
		14. NUMBER OF PAGES 19
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Authorized for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Marine pollution Atomic absorption Heavy metals San Diego Bay Anodic stripping voltammetry Automated instrumentation		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Automated anodic stripping voltammetry (AASV) is a tool for measuring, in the field, the concentrations of copper, zinc, lead and cadmium in marine waters. Measurements can be made within 10 to 15 minutes. Results obtained by AASV were compared to those obtained by atomic absorption spectrophotometry and were found to be the same within experimental error.		

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SUMMARY

PROBLEM

An automated anodic stripping voltammetry (AASV) system developed at the Naval Ocean Systems Center is capable of measuring zinc, copper, lead and cadmium at part per billion levels in seawater during field surveys and in the laboratory. In order to show the validity of the values obtained by the AASV system, the AASV results were compared to the more conventional, accepted analytical procedure of atomic absorption spectrophotometry. The AASV system was tested in San Diego Bay to determine its usefulness for routine marine environmental monitoring.

RESULTS

Concentrations of copper, zinc, and lead in unfiltered seawater measured by AASV and atomic absorption spectrophotometry were essentially the same within experimental error. The coefficient of correlation between the two procedures was 0.84 for copper, 0.89 for zinc, and 0.77 for lead. San Diego Bay surveys demonstrated the reliability and effectiveness of the AASV system for routine marine pollution monitoring. Slight increases in concentrations of copper, zinc, lead and cadmium are readily detectable above background levels.

RECOMMENDATIONS

Automated anodic stripping voltammetry should become a routine, accepted procedure for the analysis of copper, zinc, and lead in seawater for environmental monitoring. The AASV system should be used in other bays and harbors to understand the relative contribution of heavy metals from Naval ships and Naval shore facilities, as well as from private vessels and industrial sources.

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CONTENTS

INTRODUCTION . . .	page 3
PRINCIPLES OF ANODIC STRIPPING VOLTAMMETRY . . .	3
AUTOMATED ANODIC STRIPPING VOLTAMMETRY (AASV) COMPARED TO OTHER TECHNIQUES FOR MEASURING HEAVY METALS IN SEAWATER . . .	4
ANALYTICAL PROCEDURES . . .	5
EXPERIMENTAL FINDINGS . . .	7
DISCUSSION . . .	12
CONCLUSIONS . . .	13
REFERENCES . . .	14
APPENDIX A: PRECONCENTRATION OF COPPER AND ZINC FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY . . .	15
APPENDIX B: PRECONCENTRATION OF LEAD FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY . . .	16
APPENDIX C: INTERCOMPARISON DATA FOR COPPER . . .	17
APPENDIX D: INTERCOMPARISON DATA FOR ZINC . . .	18
APPENDIX E: INTERCOMPARISON DATA FOR LEAD . . .	19

INTRODUCTION

Anodic stripping voltammetry is a rapid analytical procedure to measure several of the important heavy metals in seawater at parts per billion (ppb) levels. Heavy metals are of importance in marine environmental monitoring because of the potential toxicity to marine life and to man as a consumer of "polluted" organisms. Currently, copper, zinc, lead, and cadmium are successfully measured in seawater by anodic stripping voltammetry.

By the development of the tubular graphite electrode at the Naval Ocean Systems Center (NOSC), San Diego, an automated, continuous-flow-through system for anodic stripping voltammetry became possible. The automated anodic stripping voltammetry (AASV) system which resulted provided a unique survey tool for marine environmental monitoring.

The AASV system is useful in environmental monitoring since analytical results are obtained continuously every 10 to 15 minutes for copper, cadmium, lead, and zinc. This near real-time analytical capability is unique to AASV and is desirable for directing on-going survey strategy to identify sources of pollution. Also, contamination errors are minimized with AASV since the water to be analyzed is pumped directly from the sea into the AASV system and is not subjected to the handling characteristics of conventional analytical procedures.

The AASV system has been used successfully to measure heavy metals in San Diego Bay, California Coastal water, and during extended oceanographic cruises.

PRINCIPLES OF ANODIC STRIPPING VOLTAMMETRY

Anodic stripping voltammetry involves the concentration of the positively charged heavy metal ions on a suitable negatively charged electrode followed by "stripping" of the heavy metals from the electrode. The electrode consists of a mercury drop or a mercury film on a graphite surface. Mercury is necessary for anodic stripping to occur because copper, cadmium, lead, and zinc form amalgams with mercury which are reversible. That is, after the heavy metals have been concentrated on the negatively charged mercury surface, the heavy metals can be liberated back into solution as the electrode is given a positive charge. The electrode is thus "stripped" of the heavy metals as oxidation to the component ion occurs. Each heavy metal is oxidized at a characteristic potential. The current produced at the specific potential is related to the concentration of the heavy metal in the original solution. Standard additions of known concentrations are made to the sample and thus provide for quantification of the unknown sample.

The tubular mercury graphite electrode developed at the Naval Ocean Systems Center, San Diego, made possible a continuous-flow, automated, anodic stripping system. A mercury film is deposited inside a graphite tube by electrolysis of mercuric nitrate. The automated system is controlled by a programmer, which controls a potentiostat, a recorder, two peristaltic pumps, and five solenoid-operated valves. The pumps and valves alternately circulate a mercuric nitrate solution to produce the mercury film on the graphite electrode, followed by seawater sample. The heavy metals in the seawater sample form an amalgam with the mercury film, followed by oxidation of the mercury film and quantification of the heavy metal concentrations as the current peaks are plotted on a recorder.

The ASSV system automatically collects and analyzes seawater from aboard ship or in the laboratory. The system simultaneously measures zinc, cadmium, and lead or cadmium, lead, and copper. Zinc and copper are best measured separately because of a mutual interference. For the analysis of zinc, cadmium, and lead, a plating potential of -1.6 V is used and a potential of -1.0 V for cadmium, lead, and copper (Ref. 12).

The actual AASV system used to obtain the data for this report is shown in Fig. 1, while a more complete technical description of the system can be found in several NOSC publications (Refs. 6, 11, 12).

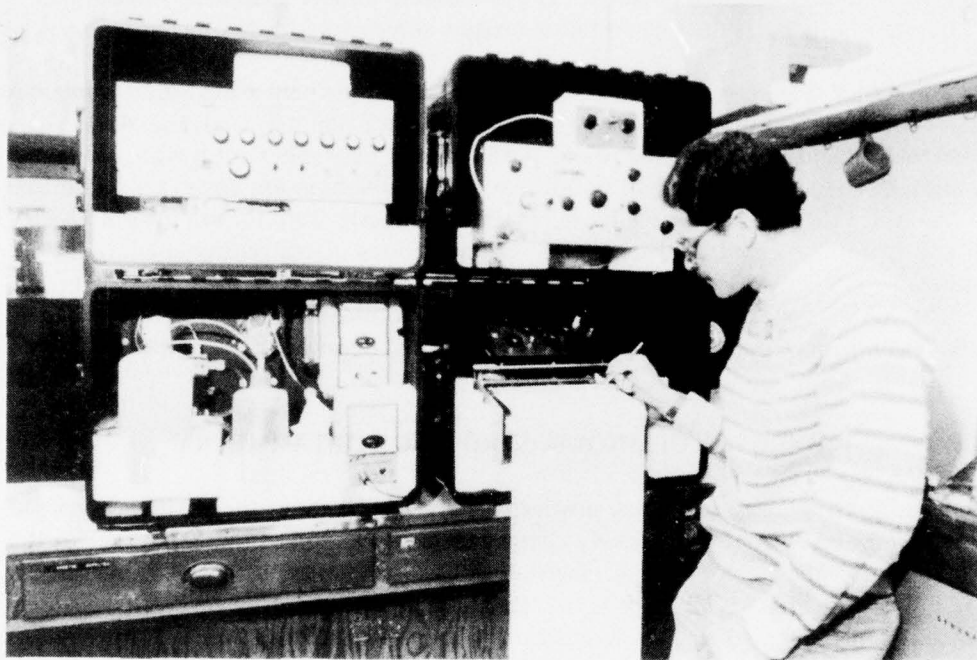


Figure 1. The automated anodic stripping voltammetry system used in the laboratory and aboard ship for marine environmental monitoring.

AASV COMPARED TO OTHER TECHNIQUES FOR MEASURING HEAVY METALS IN SEAWATER

Heavy metals in seawater are generally measured by colorimetry or by atomic absorption spectrophotometry (AA). In colorimetry, the desired heavy metal is complexed with a specific reagent and concentrated by solvent extraction. The extracted colored complex is measured on a spectrophotometer and compared to standard additions of the particular heavy metal to determine the concentration in the unknown sample.

Atomic absorption spectrophotometry is often considered the most reliable analytical procedure for the routine analysis of heavy metals because of its specificity.

However, the low concentrations of heavy metals in seawater require that preconcentration steps be employed before analysis by AA. Preconcentration can be accomplished by passing several liters of seawater through an ion-exchange resin to retain the desired heavy metal(s) (Refs. 1,8). The metal(s) are eluted from the ion-exchange column and measured on the AA. Preconcentration for AA can also be accomplished by complexation and solvent extraction as employed in colorimetry, or by co-precipitation (Refs. 2, 9).

The main advantage of AA is that most heavy metals can be measured after suitable preconcentration of the sample, while AASV is currently limited to copper, cadmium, lead, and zinc. The main disadvantage of AA for the analysis of heavy metals in seawater is the time required for preconcentration of the sample. Further, when working in the ppb range, background contamination is a serious problem during preconcentration procedures. AASV, on the other hand, virtually eliminates background contamination, and requires no preconcentration.

In order to show the validity of a new analytical procedure, such as AASV, for marine environmental monitoring, it is desirable to compare the new procedure to a more conventional, accepted procedure. Thus, a study was performed to intercompare the analytical results obtained from AASV for copper, lead, and zinc with the results obtained by the more conventional procedure of atomic absorption spectrophotometry. Cadmium was not included in the intercomparison; however our cadmium values for San Diego Bay were compared to values obtained for other bay water by another laboratory.

ANALYTICAL PROCEDURES

Since copper, zinc, and lead are usually present in seawater at concentrations below 5 ppb, it is necessary to concentrate the metals before analysis by atomic absorption spectrophotometry. Copper and zinc can be analyzed by flame atomization atomic absorption spectrophotometry after a seven hundredfold concentration using a cation exchange resin and freeze-drying (Appendix A).

For lead analysis, a two-column ion-exchange resin procedure was developed (Appendix B). Because of the limited sensitivity of atomic absorption spectrophotometry in the flame mode to low lead concentrations, a graphite furnace was used to obtain the needed extra sensitivity. However, the eluate from the cation-exchange resin contained high concentrations of sodium in addition to the desired heavy metals. The high sodium concentrations made analysis in the graphite furnace impractical because of enormous errors produced by "splattering" of the sodium within the graphite tube.

A procedure was thus developed using a second column in order to separate the lead from sodium. The cations eluted from the cation-exchange column in 2N HCl were passed through an anion-exchange resin that selectively retains lead and excludes sodium when in a 2N HCl matrix. This can be accomplished because in high chloride concentrations, lead exists as the anion PbCl_4^{-2} . Lead is subsequently eluted from the anion-exchange column with 8N HCl. Lead in the 8N HCl matrix can be analyzed successfully in the graphite furnace of the atomic absorption spectrophotometer.

WATER SAMPLES

Water samples were collected by pumping water continuously from San Diego Bay at the NOSC facility through tygon tubing with a peristaltic pump. San Diego Bay water

was analyzed at 10- to 15-minute intervals with the AASV apparatus using 1-liter sample portions. In between AASV analyses, 4-liter samples were collected in acid-washed polyethylene bottles for concentration on ion-exchange resin and analysis by atomic absorption spectrophotometry. The 4-liter sample portions were frozen until analyses were performed.

Five additional water samples for copper analyses were collected at the municipal pier of the city of Oceanside, Calif., at the Scripps Institution of Oceanography Pier, San Diego, and several miles off the California coast between San Diego and Oceanside.

The surveys of San Diego Bay were conducted from a modified landing craft operated by NOSC. Water was pumped through a tygon tube below the sea surface and analyzed by AASV every 10 to 15 minutes.

AUTOMATED ANODIC STRIPPING VOLTAMMETRY (AASV)

The AASV system is readily portable for survey use and has been described in detail (Refs. 6, 11, 12). The system utilizes a tubular graphite electrode through which a mercury solution is circulated to deposit a mercury film. The mercury deposition potential is also the deposition potential of the 1-liter seawater sample. A potential of -1.6 V vs Ag/AgCl was used for the electrolysis of zinc, and -1.0 V vs Ag/AgCl for the concurrent deposition of lead, cadmium, and copper.

ATOMIC ABSORPTION SPECTROPHOTOMETRY (AA)

Copper and zinc measurements were performed on a Perkin-Elmer Model 306 instrument using an air-acetylene flame. Concentrations were calculated by comparison with standard copper and zinc solutions in a 2N HCl matrix and correcting for the analysis blank.

For lead analyses the Perkin-Elmer Model 306 was used with the graphite furnace. Samples were compared with standard lead in 8N HCl solutions and the analysis blank subtracted.

ANALYSIS BLANKS

Copper and zinc were removed from 4-liter seawater samples by passage through the cation-exchange column. This "copper-and-zinc-free seawater" was subsequently passed through a regenerated cation-exchange column, eluted, freeze-dried, redissolved in 5 ml 2N HCl, and otherwise treated identically to the samples. The 5 ml 2N HCl produced a total volume of 5.6 ml when added to the freeze-dried salts. This 5.6-ml portion constituted the reagent and analysis blank for copper and zinc.

The lead blank was prepared by passing a 4-liter seawater sample through the cation-exchange column to remove all the lead measurable by this method. This "lead-free seawater" was subsequently passed through a regenerated cation-exchange column and eluted with 100 ml of 2N HCl. One hundred ml of HCl eluate was passed through the anion-exchange column and eluted with 30 ml of 8N HCl. Thirty ml of 8N HCl eluate constituted the lead analysis blank.

EXPERIMENTAL FINDINGS

The results of the intercomparison of AASV and AA for copper, zinc, and lead are presented in Figs. 2-4. The raw data for these correlations are presented in Appendixes C, D, and F.

Twelve comparisons were performed for copper (Fig. 2). A linear regression of the twelve points yields a slope of 0.84 and an intercept of 0.12, with a correlation coefficient of 0.84. If the most aberrant point is neglected, the slope becomes 1.03, the intercept 0.04, and the correlation coefficient increases to 0.91. Thus, within experimental error the values obtained by the two methods are identical.

Twenty-two intercomparisons of the two methods were performed for zinc (Fig. 3). A linear regression of the data gave a slope of 1.07, an intercept of -0.20, and a correlation coefficient of 0.89. As with copper, the zinc values exhibited no systematic difference between the values obtained by AASV and AA.

Figure 4 shows the linear regression for 30 intercomparisons of lead. The slope was 0.82, the intercept 0.08, and the correlation coefficient 0.77. The lead intercomparison exhibited greater scatter than the copper and zinc intercomparisons; however, the results still show AASV and AA to be within experimental error.

Figures 5 and 6 show the results of the San Diego Bay surveys using the AASV system aboard ship. Values for zinc ranged from 0.7 to 2.9 ppb, cadmium and lead both ranged from 0.1 to 0.4 ppb, and copper ranged from 0.7 to 2.4 ppb.

Figures 7, 8 and 9 show lead, cadmium, and zinc concentrations determined by AASV in relation to tidal cycle. There was essentially no change in lead and cadmium concentrations during a complete tidal cycle. Lead remained at 0.15 ppb and cadmium at 0.10 ppb. Zinc, however, showed a correlation with tidal cycle. Zinc values were highest at low tide and lowest at high tide.

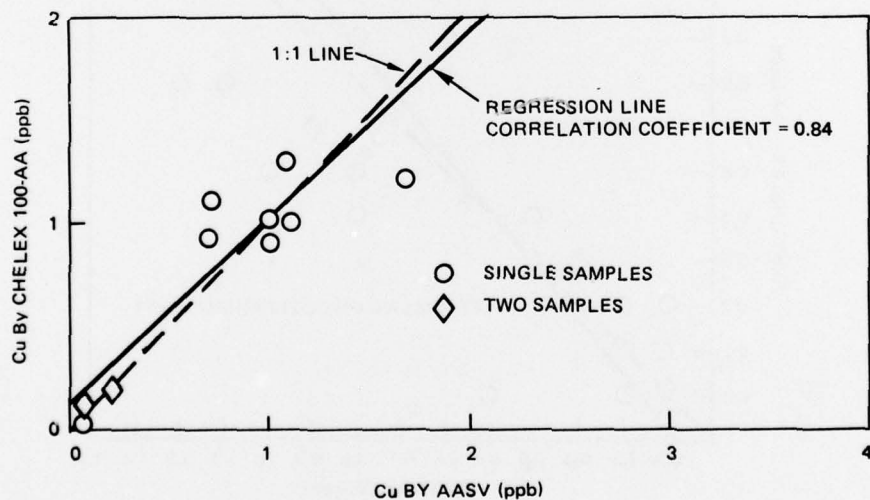


Figure 2. Copper intercomparison by AASV and AA.

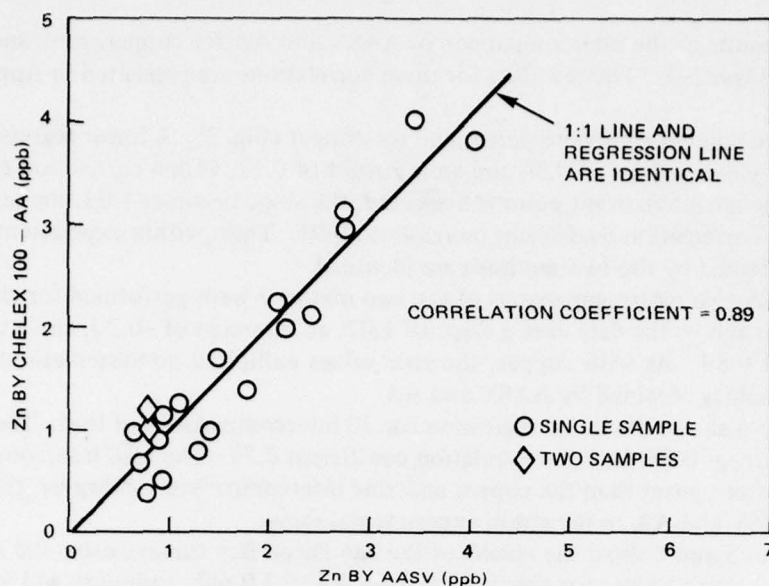


Figure 3. Zinc intercomparison by AASV and AA.

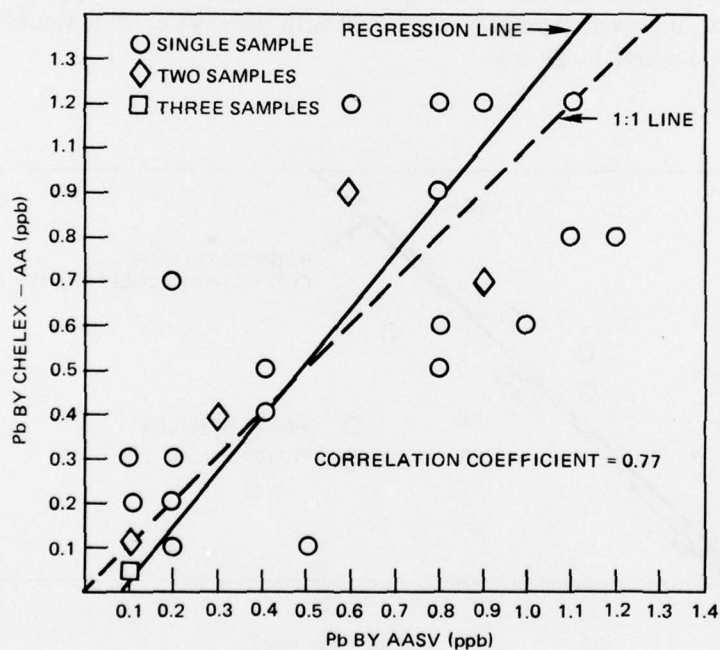


Figure 4. Lead intercomparison by AASV and AA.

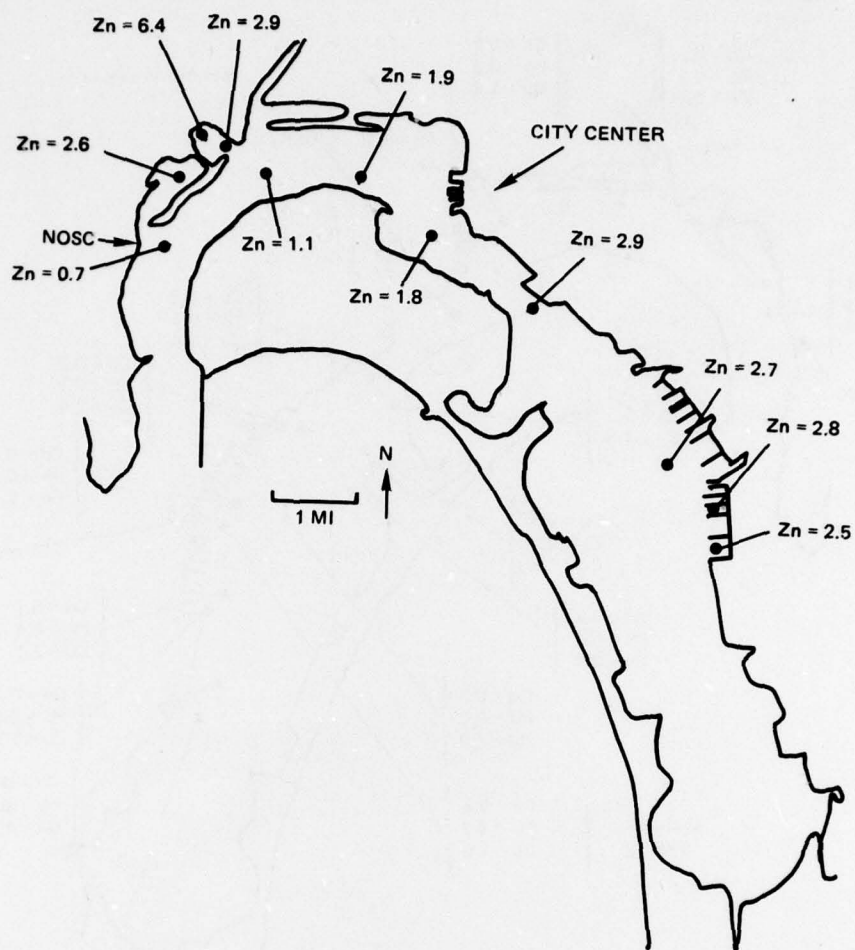


Figure 5. San Diego Bay survey (14 October 1975) for zinc by means of AASV. Concentration values are in parts per billion.

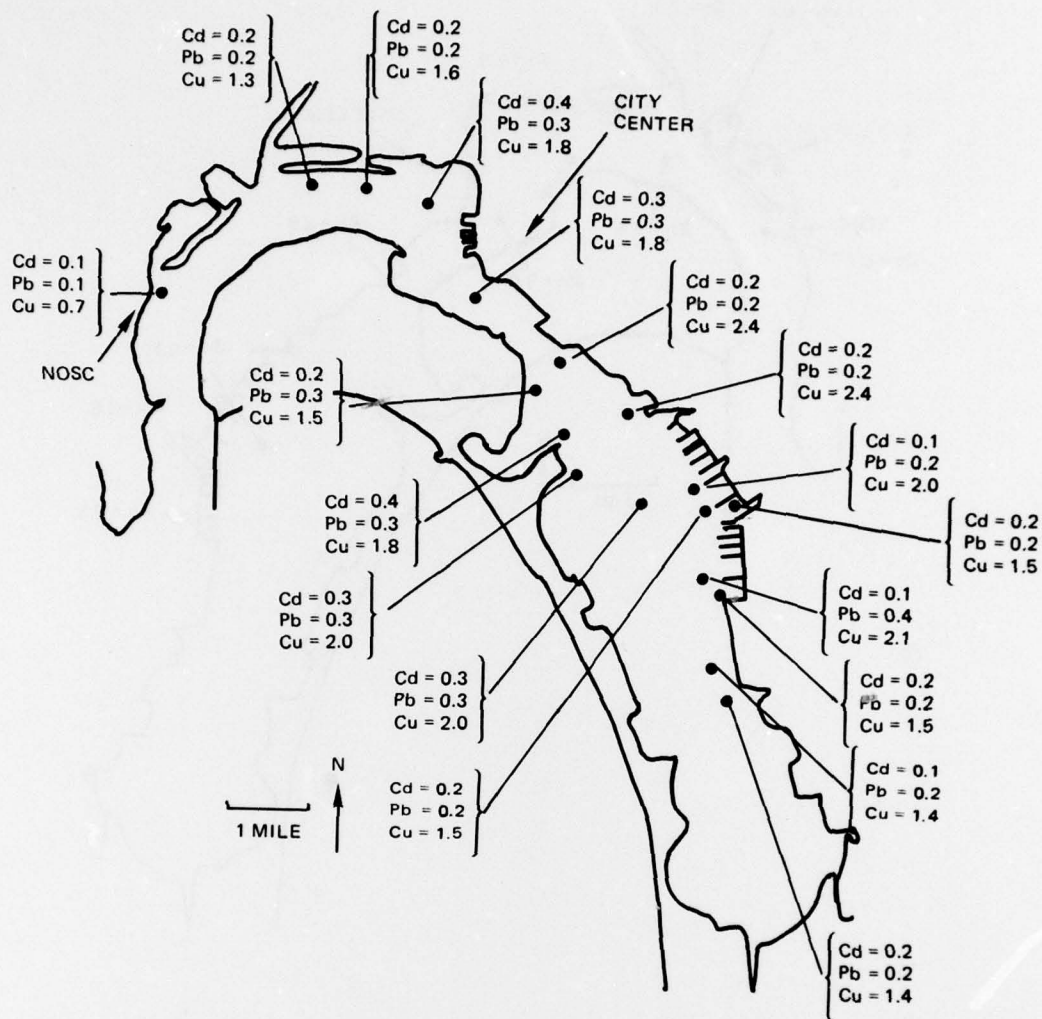


Figure 6. San Diego Bay survey (21 January 1976) for copper, cadmium, and lead by means of AASV. Concentration values are in parts per billion.

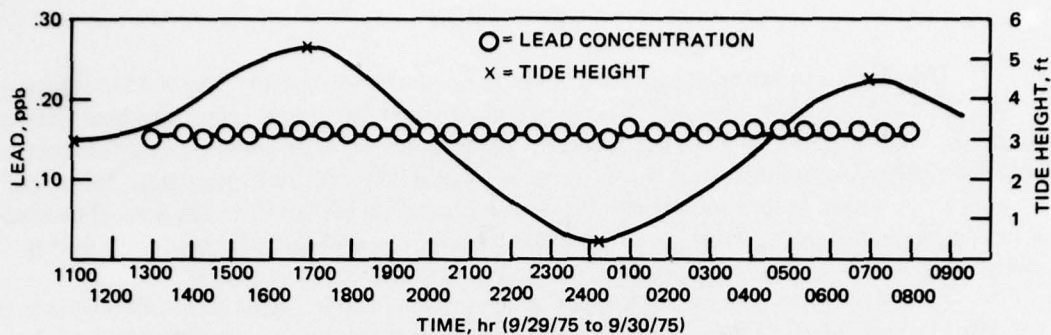


Figure 7. Relationship between lead concentrations and the tidal cycle at NOSC sampling station, near the mouth of the San Diego Bay.

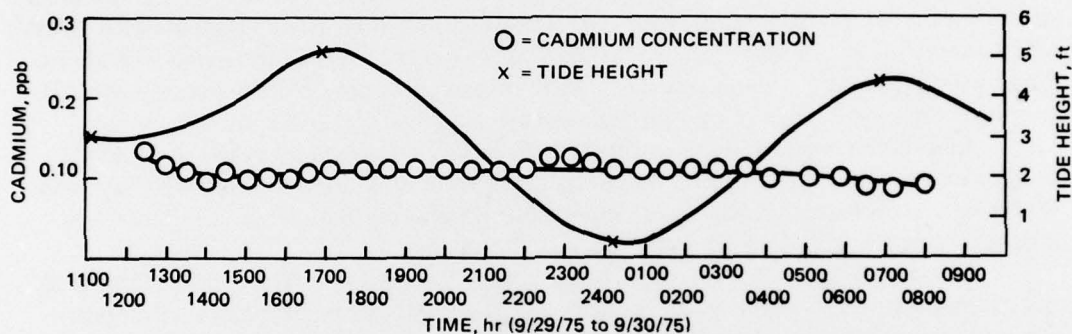


Figure 8. Relationship between cadmium concentrations and tidal cycle at NOSC sampling station, near the mouth of the San Diego Bay.

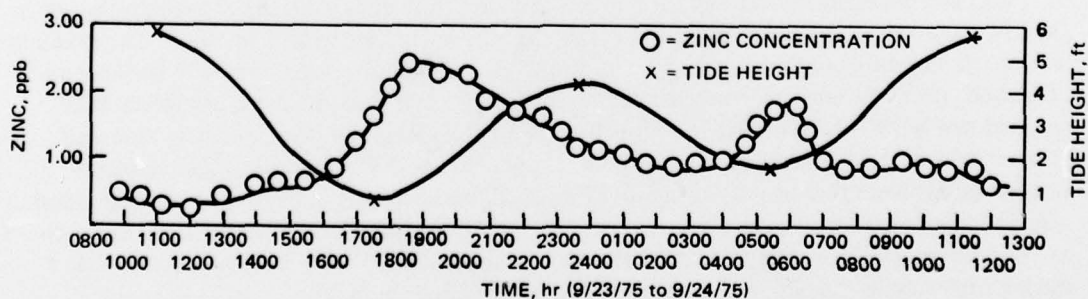


Figure 9. Relationship between zinc concentrations and tidal cycle at NOSC sampling station, near the mouth of the San Diego Bay.

DISCUSSION

The intercomparison values for copper, zinc, and lead measured by AASV compared closely to values produced by AA. The intercomparisons for copper, zinc, and lead showed correlation coefficients of 0.84, 0.89, and 0.77, respectively. The lower correlation coefficient for lead is likely a result of the extreme low solubility of lead in seawater. Most lead in seawater is likely bound to particulates or exists as insoluble lead precipitates. The lead-bound particulates or precipitates are probably solubilized with greater variability during analysis by AASV or AA, thus producing the lower correlation coefficient.

The comparison studies for copper, zinc, and lead show AASV and AA to be identical within experimental error. AASV is thus a more rapid analytical procedure for marine pollution monitoring and environmental survey work than any other procedures currently available.

There is a limited amount of data in the literature for intercomparisons of AASV and other techniques and for heavy metal concentrations within San Diego Bay. A zinc intercomparison study using a mercury thin-film electrode AASV system produced values similar to ion-exchange resin extraction and AA analysis (Ref. 4). Lead values within San Diego Bay were found to be 0.16 ppb using isotope dilution to determine yields and mass spectrometry for quantification (Ref. 10). This value is similar to our findings with AASV, which showed lead to range from 0.1 to 0.4 ppb within the bay. Copper values of about 2 ppb were reported for water near the mouth of San Diego Bay by AA analysis (Ref. 7), and were within the range of our copper values determined by AASV within the bay.

Cadmium concentrations within San Diego Bay measured by AASV during our surveys ranged from 0.1 to 0.4 ppb. No comparative cadmium data for San Diego Bay were available; however similar values were reported for Monterey Bay, where cadmium was shown to range from 0.1 to 0.3 ppb (Ref. 5).

Our San Diego Bay surveys revealed concentration values for copper, zinc, lead, and cadmium to be lowest near the mouth of the bay. Mixing of bay water with open-ocean water accounts for the relatively lower heavy metal concentrations near the mouth of the bay compared to the higher concentrations within the bay. Higher concentrations of these metals within the bay are attributable to the presence of ships (Ref. 13). Copper is found in antifouling ship coatings and in brass. Zinc is used for galvanizing and as a sacrificial anode for cathodic protection in corrosion control. Lead is also used in cathodic protection, in paints, and as a ballast material. Cadmium is used as a corrosion-resistant coating to protect iron exposed to seawater.

The concentration values for copper and zinc showed a substantial gradient between the low values near the mouth of the bay and locations further within the bay. The gradient was much less, however, for lead and cadmium. Because of the small gradient for lead and cadmium, no difference in concentration values was measured during a complete tidal cycle at the NOSC station near the mouth of San Diego Bay. On the contrary, zinc and copper showed a dramatic correlation to tidal cycle at the NOSC station. Zinc concentration values were maximum during low tide and lowest during high tide. A similar trend was demonstrated for copper (Ref. 13). Zinc and copper values increased during low tide as "contaminated" water from within the bay passed by the NOSC station and decreased during high tide as "clean" open-ocean water moved into the bay.

A noteworthy consideration in the analysis of heavy metals in seawater is the form of the heavy metal, and what form(s) each analytical procedure actually measures. Heavy metals exist as free ions, bound to dissolved organic matter or bound to suspended organic or inorganic particles. Different analytical techniques measure different portions of the

total heavy metals present. AASV measures the free ionic form of the heavy metal in addition to the various bound forms capable of being liberated by the electrical potential of the AASV electrode. To use AASV to measure the greatest amount of bound heavy metals, the sample can be acidified. When the sample is acidified prior to electrolysis, additional quantities of metals are liberated from particulates and organic ligands.

AA measures essentially all the heavy metal placed into the instrument; however, during the preconcentration steps, metals may be added by contamination or lost owing to incomplete concentration. According to Florence and Batley (Ref. 3) only a fraction of the total copper and zinc content of seawater is retained by the ion-exchange column used for preconcentration. Also, unfiltered seawater from near-shore contains considerable sediment material, particularly after agitation of the water by rough weather.

Sediments contain high concentrations of heavy metals, which may be leached by the acid treatment during the preconcentration step on the ion-exchange column. The high concentration of heavy metals attached to the sediments would be filtered onto the surface of the ion-exchange column and leached during acid elution of the column. This would give abnormally high heavy metal values since sediments would be measured in addition to the water.

It is interesting and significant that our intercomparison study revealed such close agreement between AASV and AA analysis of identical water samples, considering that each technique may be measuring different percentages of the different forms of a particular heavy metal. This suggests that AASV is thorough in extracting bound heavy metals from seawater. An exception would likely occur when very large amounts of sediments are present in the water. This was suggested during the first four lead intercomparisons on 4/13/77 (Appendix E). The AA values were 2 to 3 times higher than corresponding AASV values, probably due to the large amount of sediment collected with the water samples.

When samples contain large amounts of suspended solids, discretion should be exercised when interpreting results for unfiltered seawater obtained by either AASV or AA. It may be the suspended sediments that are being measured, thus giving higher concentrations of heavy metals than is actually the case.

Our surveys in San Diego Bay have tested the application of the AASV system for portable field use. The AASV system readily measures ambient concentrations of copper, zinc, lead, and cadmium and indicates areas of higher concentrations. The ability to show slight gradients in heavy metal concentrations is essential in tracing sources of heavy metal contamination. The AASV system has consistently demonstrated this capability. The portability of the AASV system, the 10- to 15-minute time for analysis of several heavy metals concurrently, the minimization of contamination errors by eliminating preconcentration procedures and handling are all unique features of the AASV system that can not be overemphasized.

CONCLUSIONS

An intercomparison of analytical results for copper, zinc, and lead in unfiltered seawater produced by automated anodic stripping voltammetry (AASV) and atomic absorption spectrophotometry (AA) shows the two techniques to be similar within experimental error. Thus, AASV is as reliable as AA and an analytical tool for measuring these heavy metals in unfiltered seawater.

Environmental surveys in San Diego Bay with AASV have demonstrated its unique capability for marine pollution monitoring. Currently AASV is the only portable survey tool available which can measure copper, cadmium, lead, and zinc within 10- to 15-minutes.

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APPENDIX A: PRECONCENTRATION OF COPPER AND ZINC FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY

Four-liter water samples were passed through cation-exchange resin of the imino-diacetic acid exchange group type in the ammonium form at a flow rate not greater than 5 ml/min (Chelex 100, mesh 50-100, BioRad Laboratories, Richmond, Calif).

The columns were constructed of Pyrex glass 30 cm high and the resin occupies the lower 15 cm of the 1.5-cm-ID column. The upper part of the column has an expanded diameter capable of receiving the neck of the narrow-mouth 4-liter polyethylene bottle containing the 4-liter seawater sample. Packing of the column was accomplished by forming a slurry from approximately 25 ml of the resin and pouring into the column. Before 4-liter water samples were added to the column, the column was cleaned and regenerated by the addition of the following in this order: 100 ml quartz distilled dionized water (QD_2H_2O), 60 ml 2N HCl, 100 ml QD_2H_2O , 60 ml 2N NH_4OH , and 100 ml QD_2H_2O .

Following passage of the 4-liter sample through the resin bed in the ammonium form, the column is rinsed with 100 ml (four bed volumes) of QD_2H_2O . Elution of heavy metals from the column is achieved with 60 ml 2N HCl followed by 40 ml QD_2H_2O for a total volume of 100 collected in a 250-ml Teflon bottle. The eluate is reduced to dryness by freeze-drying and redissolved in 5 ml of 2N HCl (resultant volume = 5.6 ml). The final 5.6-ml portion represents a concentration of 714 from the original 4-liter seawater sample. This portion is used for Cu and Zn analysis in the atomic absorption spectrophotometer.

Following elution with 2N HCl and QD_2H_2O , the column is rinsed with an additional 60 ml QD_2H_2O , recharged with 60 ml 2N NH_4OH , and rinsed with 100 ml QD_2H_2O before adding further 4-liter seawater samples.

Both Cu and Zn were shown to be recovered in excess of 98% by the procedure (Ref. 13).

APPENDIX B: PRECONCENTRATION OF LEAD FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY

A two-column system was used to prepare lead for analysis in the graphite furnace of the atomic absorption spectrophotometer. The first concentration step used the same cation-exchange resin used for copper and zinc. The only difference in the lead procedure is that 100 ml of a 2N HCl was added to elute the column rather than 60 ml 2N HCl and 40 ml $\text{QD}_2\text{H}_2\text{O}$. Before reactivating the cation-exchange column with 60 ml 2N NH_4OH , the column was rinsed with 100 ml $\text{QD}_2\text{H}_2\text{O}$.

The 100 ml 2N HCl eluate from the cation-exchange column was passed through an anion-exchange resin (AG 1-X10, 100-200 mesh, BioRad Laboratories, Richmond, Calif.) in the chloride form. The anion-exchange column consisted of a pyrex glass column (480 mm long, 5 mm ID) with a column volume of 12.5 ml. The upper part of the column has an expanded diameter capable of receiving the 100 ml of eluate from the cation-exchange column. Before the anion-exchange column was initially used it was eluted with 30 ml of 8N HCl and regenerated with 30 ml 2N HCl. Flow rates of less than 1 ml/min through the column were maintained by attaching a peristaltic pump at the end of the column. The column was rinsed with 20 ml 2N HCl after passage of the 100-ml sample and eluted with 30 ml 8N HCl into 250-ml Teflon bottles for analysis in the graphite furnace of the atomic absorption spectrophotometer. The 30 ml of eluate from the anion-exchange column was 133 times more concentrated than the original 4-liter seawater sample. The column was regenerated with 30 ml 2N HCl before the addition of the next sample.

To demonstrate the quantitiveness of the two-column concentration procedure, 4-liter seawater samples were spiked with unknown concentrations of lead. The spiked seawater had previously been cleansed of lead by passage through Chlex-100 resin. The spiked seawater samples were passed through Chelex-100 resin and the eluate passed through Chelex AG-1 resin. The final eluate from the Chelex AG-1 column showed a lead recovery in excess of 85%.

APPENDIX C: INTERCOMPARISON OF DATA FOR COPPER

<u>Date</u>	<u>Location</u>	<u>Automated Anodic Stripping Voltammetry, ppb</u>	<u>Atomic Absorption Spectrophotometry, ppb</u>
2/20/75	S.D. Bay Water	2.0	0.9
3/4/75	S.O. Cruise Oceanside Pier	0.2	0.2
3/4/75	S.O. Cruise Coastal Water	0.05	0.1
3/5/75	S.O. Cruise Coastal Water	0.05	0.1
3/6/75	S.O. Cruise Coastal Water	0.05	0.0
4/2/75	Scripps Water	0.2	0.2
4/3/75	S.D. Bay Water	1.7	1.2
4/11/75	S.D. Bay Water	1.0	1.0
4/17/75	S.D. Bay Water	0.7	0.9
4/21/75	S.D. Bay Water	1.1	1.3
5/1/75	S.D. Bay Water	1.1	1.0
5/1/75	S.D. Bay Water	0.7	1.1

APPENDIX D: INTERCOMPARISON DATA FOR ZINC*

<u>Date</u>	<u>Time</u>	<u>Automated Anodic Stripping Voltammetry, ppb</u>	<u>Atomic Absorption Spectrophotometry, ppb</u>
5/29/75	1530	1.3	1.8
5/30/75	0800	4.1	3.8
5/30/75	1430	3.5	4.0
6/10/75	1630	2.1	2.2
6/11/75	0820	2.8	3.0
6/11/75	1245	1.5	1.7
6/11/75	1530	2.2	2.0
6/12/75	0745	2.8	3.1
6/13/75	1540	1.1	1.2
8/26/75	1040	0.8	1.0
8/26/75	1115	0.7	1.0
8/26/75	1330	0.8	1.0
9/5/75	1535	0.9	0.9
9/5/75	1600	0.9	0.5
9/23/75	1715	1.4	1.0
9/23/75	1737	1.8	1.4
9/23/75	1821	2.4	2.1
10/9/75	1325	0.7	0.7
10/9/75	1350	0.8	0.4
10/9/75	1400	0.8	1.1
10/9/75	1430	0.8	1.1
10/9/75	1440	0.9	1.1

*All water samples were collected in San Diego Bay near the NOSC facility.

APPENDIX E: INTERCOMPARISON DATA FOR LEAD

Date	Time	Automated Anodic Stripping Voltammetry, ppb	Atomic Absorption Spectrophotometry, ppb
3/10/76	1340	1.2	0.8
"	1355	1.1	1.1
"	1405	1.1	0.8
"	1430	1.0	0.6
"	1440	0.9	0.7
"	1505	0.8	0.6
"	1525	0.8	0.5
3/11/76	0937	0.5	0.1
"	1015	0.6	0.9
"	1030	0.6	0.9
"	1054	0.6	1.1
4/13/76	1450*	0.8	3.2
"	1500*	0.8	2.3
"	1510*	0.9	1.3
"	1520*	0.9	2.0
"	1530	0.9	1.1
"	1537	0.9	0.7
"	1545	0.8	0.9
"	1555	0.8	1.1
6/29/76	1438	0.2	0.1
"	1448	0.2	0.2
"	1458	0.2	0.3
"	1508	0.2	0.7
"	1518	0.3	0.4
"	1528	0.3	0.4
6/30/76	1345	0.4	0.4
"	1435	0.4	0.5
10/15/76	1005	0.1	0.4
"	1015	0.1	0.1
"	1025	0.1	0.05
"	1035	0.1	0.05
"	1045	0.1	0.1
"	1105	0.1	0.05
"	1115	0.1	0.02

All water samples were collected in San Diego Bay near the NOSC facility.

*The values identified by an asterisk were not used in the correlation analysis between AASV and AA because abnormally high amounts of suspended solids were present.